The infrared spectra of several rare-earth formates

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Table 1. IR spectra of the ligand (BADO) and complex [(Cu(BADO)$_2$] molecules

BADO (cm^{-1})	Strength and shape	Assignment and remarks	Assignment and remarks	Strength and shape	Cu(BADO)$_2$ (cm^{-1})
3400 3150	broad	O–H vibrations and H- bond	O–H vibrations and H-bond (2 types)	broad (symmetric)	3400
1620		C=N stretching	C=N stretching after complexation and conjugation		1600
1580 1560 doublet	strong weak	quadrupole str. of benz. ring and C=O or C=N	quadrupole str. of benz. ring and C=O or C=N	strong weak	1580 1560
1440 1400 doublet	strong weak (symmetric)	semicircle str.	semicircle str.	strong (asymm.)	1450 1410
1020	medium (broad)	N–O group	N–O group vibr. following changes in the character of N–O bond	medium (narrow)	1025 995 920
930	strong (broad)	vibration			
690	strong (symm)	out of plane bending (benz. ring)	out of plane bending (benz. ring)	strong (asymm.)	700

Finally, it is interesting to note that there is no NMR evidence for the existence of isomeric (tautomeric) mixtures in the case of AADO in D_2O solution.

(b) *IR spectra of* BADO *and* Cu(II)-(BADO)$_2$. *Table 1* shows the important features of the IR spectra of the BADO and Cu(II)BADO molecules.

The *pseudoaromatic conjugated system* in the copper chelate is shown by the following:

(a) A shift in the C=N stretching mode of the free ligand from 1620–1600 cm^{-1} (in the complex).

(b) A change in the stretching vibration bands characteristic of N–O (single bond) in the free ligand (930–1020 cm^{-1} range) due to a change in the character of the N–O bond, owing to complexation.

As for the existence of *hydrogen bonding* in both ligand and complex species:

(1) The i.r. spectrum of the free ligand (3125–3550 cm^{-1} range) suggests the possibility of two kinds of hydrogen bonds, O–H...N and O–H...O (see also NMR data above), in the Cu(BADO*)$_2$ complex, one kind only is apparently present (O–H...O).

(2) An inductive effect of the benzene group on the O–H stretching vibrations, as shown by the shift of the related frequencies to higher wavelength, is compared with the corresponding AADO and Cu–AADO spectra.

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THE IR spectra in the range of 4000–100 cm^{-1} of the following rare-earth formates were studied: Ce(HCOO)$_3$, Pr(HCOO)$_3$, Nd(HCOO)$_3$, Nd(HCOO)$_3$, Sm(HCOO)$_3$, Eu(HCOO)$_3$ and Gd(HCOO)$_3$. The influence of the metal ion on the metal–oxygen stretching frequencies has been investigated. A normal coordinate analysis of the crystal as a whole will be given elsewhere as well as the potential energy distribution among the force constants for each lattice vibration for these rare-earth formates.

Table 1. Vibrational spectra and assignments of the rare-earth formates $M(HCOO)_3$ (values in cm^{-1})

$Ce(HCOO)_3$	$Pr(HCOO)_3$	$Nd(HCOO)_3$	$Sm(HCOO)_3$	$Eu(HCOO)_3$	$Gd(HCOO)_3$	assignments
2900 (w)	2900 (w)	2900 (w)	2900 (w)	2900 (w)	2908 (w)	ν_1 C-H stretching
	2820 (w)					$\nu_5 + \nu_5^1$
	2025 (w)					$\nu_2^1 + \nu_5 - \nu_3$
1590 (b,s)	1592 (b,s)	1582 (b,s)	1581 (b,s)	1580 (b,s)	1585 (b,s)	ν_4 C-O asym-stretch
1423 (m)	1423 (m)	1422 (w)	1430 (m)	1427 (m)	1430 (m)	ν_5
1400 (m)	1400 (m)	1400 (m)	1409 (m)	1409 (m)	1411 (m)	ν_5^1 δ(C-H)
1383 (m)						ν_2
1351 (m)	1352 (s)	1345 (s)	1352 (m)	1352 (m)	1355 (m)	ν_2^1 C-O sym-stretch
	1108 (m)					ν_6 π(H) wagging
776 (s)	772 (s)	776 (s)	779 (s)	779 (s)	784 (s)	ν_3
				775(sh,w)		ν_3^1 δ(O-C-O)
276 (s)	280 (s)	284 (s)	289 (s)	290 (s)	297 (s)	ν_7 M-O asym-stretch
240 (m)	243 (m)	245 (m)	249 (m)	251 (m)	260 (m)	ν_8 M-O sym-stretch
162 (w)	160 (w)	160 (m)	160 (w)	159 (m)	160 (m)	ν_9
122 (m)	121 (m)	130 (m)	135 (m)	139 (m)	139 (m)	ν_{10} δ(O-M-O)

s= strong, m= medium, w= weak, b= broad and sh = band is accompanied by a shoulder.

EXPERIMENTAL

The procedure of Sohoo, Panda and Patnaik[1] was used for the preparation of the formates of rare-earth elements. It involves the reaction of the nitrates of the desired elements with formic acid. For the formates $Pr(HCOO)_3$ and $Nd(HCOO)_3$ we prepare first the chloride of these rare-earth elements by a reaction of HCl and the oxides, according to the procedures of Scheele and Cleve for $PrCl_3$ and $NdCl_3$ respectively[2, 3]. The insoluble rare-earth formates were filtered and dried at 200°C. The recrystallisation from water for all compounds required much care.

The IR spectra in the range 4000–400 cm^{-1} were obtained using the Hitachi Grating Spectrometer EPI-G3. These spectra were measured in KBr pellets. The far IR spectra (400–100 cm^{-1}) were made with a Beckman Fourier Spectrometer FS-720, using polyethylene pellets.

RESULTS AND DISCUSSION

Table 1 contains the observed frequencies and assignments. We have chosen the assignments of Ferraro and Becker[4], based on their deuteration studies of $Eu(OOCCD_3)_3$ and $La(OOCD)_3$. The assignments ν_7 and ν_8 as $\nu_{MO\text{-}asym}$ and $\nu_{MO\text{-}sym}$ respectively, are given also by them. This was corroborated by Augino[5] who found that these absorptions ν_7, ν_8 were unaffected by application of high pressures from which he concluded that these vibrations cannot be rotatory or translatory lattice vibrations. Only praseodymium formate shows all six bands of the formate ion. The other formates give five bands. The splitting of ν_2 which occurs in cerium formate and of ν_3 in europium formate, were not found in lanthanum formate, according to the measurements of Ferraro and Becker.

The clear shifts in the low-frequency absorptions indicate an increase in the metal-oxygen strength from cerium to gadolinium. Ferraro and Becker stated that the increase of the low-frequencies ν_7, ν_8 of lanthanum formate and neodymium formate is as expected for highly covalent bonding M–O if the atomic weight increases. The M–O bonding in the case of the rare-earth formates is weakly covalent however. Hannay and Smyth[6] derived a simple equation relating partial ionic character to the difference in electronegativity. We calculated for Ce–O and Gd–O bonding, 56% and 53% ionic character, respectively. We see that only a small difference between ionic character for Ce–O and Gd–O gives a distinctive shift in the frequencies 7 and ν_8.

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